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CO₂ CAPTURE by CaO IN A SOUND ASSISTED FLUIDIZED BED AT Ca-LOOPING CONDITIONS

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ABSTRACT

The Ca-Looping process is a viable technology to achieve high CO₂ postcombustion capture efficiencies (Blamey et al. (1)). This involves the separation of CO₂ by means of the carbonation reaction of CaO to capture CO₂ in a fluidized bed at high temperature, and the subsequent calcination of limestone (CaCO₃) to regenerate the sorbent. In this paper we show a study on the capture performance of a fluidized bed of CaO at Ca-looping conditions as affected by acoustic vibrations, which serve to enhance the fluidization quality and the mass/heat gas-solids transfer. As a consequence, it is shown that the CO₂ capture capacity during the fast phase of practical interest is notably increased for sound intensities and vibration frequencies of typically around 140 dB and 100 Hz, respectively.

INTRODUCTION

The Ca-Looping (CaL) process for postcombustion capture is realized in practice by means of two interconnected fluidized beds. CaO powder in a fluidized bed reacts with the CO₂ present in the gas to form CaCO₃ at temperatures typically around 650°C. The spent sorbent is then regenerated by calcining it at high temperatures (typically around 900°C) in a second fluidized bed reactor interconnected with the carbonator. In the calciner, CaCO₃ decomposes to yield CaO and a concentrated stream of CO₂ ready to be stored. In practice, the sorbent particles must react with CO₂ at low volume concentrations (of around 15%) during short contact times while ideally maintaining a high CO₂ capture capacity with the number of cycles (Blamey et al. (1), Manovic and Anthony (2)). The CaL process finds also a precombustion application in the sorption enhanced steam methane reforming (SE-SMR) process. Higher methane to hydrogen conversion and improved energy efficiency are achieved by on-line capture of CO₂ while steam methane reforming and water gas shift reactions occur (Romano et al. (3)).

Carbonation of CaO particles occurs in two phases (Grasa et al. (4)). A first fast carbonation stage is characterized by the sorption of CO₂ on the free surface of the particles. After a thin layer of CaCO₃ (between 30 and 50 nm thick (Grasa et al. (4)) covers the free surface of the sorbent particles, CO₂ sorption turns to be controlled by a much slower phase characterized by the diffusion of CO₂ through the solid CaCO₃ layer. It must be taken into account that carbonation of CaO

during the fast phase proceeds under mass/heat transfer control. Thus, the rate of CO₂ capture in the fast phase by a fluidized bed is not just controlled by the kinetics of the chemical reaction itself, but also by the transport of CO₂ and heat to the particles' surface. In this regard, carbonation can be hindered by poor and heterogeneous gas/solids contact and mass/heat transfer (Blamey et al. (1)).

We describe in the present manuscript the use of a noninvasive physical method to enhance the CO₂ capture performance of a fluidized bed of CaO at CaL conditions consisting of the application of acoustic vibration. Acoustic vibrations are useful to promote gas/solids mixing uniformity in fluidized beds by forcing particle vibrations, which reduces aggregation and disrupts gas channels thus homogenizing fluidization and increasing the gas/solids contact efficiency (Ammendola et al. (8)). On the other hand, sound waves induce a number of phenomena taking place at the gas/solids interface, such as acoustic streaming, which contribute to enhance mass/heat transfer rates in gas/solids reactors (Yarin et al. (5), Komarov et al. (6), Al Zaitone (7)). The fundamental principle is that attenuation of acoustic energy flux makes momentum flux available to force streaming motions around the solids. Accordingly, it is seen that the imposition of acoustic vibrations on a steady gas flow yields remarkable improvements in the efficiency of industrial processes such as fuel combustion, pyrometallurgical, and pollutant removal processes involving gas-solid reactions at high temperatures (Komarov et al. (6)). Altogether, the improvement of gas/solids contact efficiency in a heterogeneous fluidized bed and the enhancement of mass/heat transfer at the gas/solids interface, would serve to enhance fast capture of CO₂ in a fluidized bed carbonator at CaL conditions as it is confirmed by our experimental results.

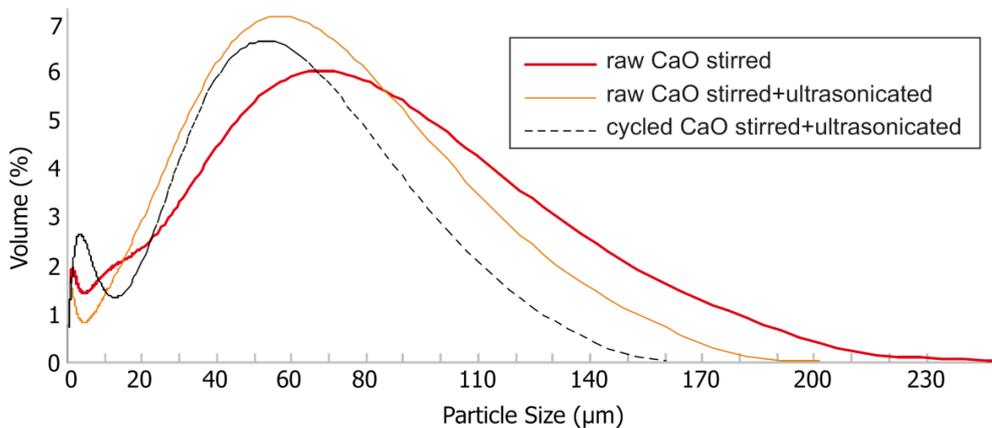


Figure 1: Particle size distribution of CaO samples suspended in isopropanol (stirred and ultrasonicated) taken before and after 1 carbonation/calcination cycle. Measurements performed by means of laser based diffractometry using a Mastersizer 2000 (Malvern Instruments).

EXPERIMENTAL SETUP AND PROCEDURE

CaO from Sigma-Aldrich (see Fig. 1 for particle size distribution measurements) has been used as CO₂ sorbent. The experimental setup used is schematized in Fig. 2. The material (100 g corresponding to a bed height of 5 cm) is placed in a 50 mm i.d. quartz reactor where it rests over a porous quartz plate that serves as gas distributor. The inlet gas flow is set to 2000 cm³/min (which is about 5 times

the minimum fluidization gas velocity) and can be switched to dry air (used for calcination) or to a mixture of 15% CO₂/85% N₂ in volume (used for carbonation) by means of mass flow controllers. The material is firstly subjected to a calcination step (T=900⁰C) for 15 min during which Ca(OH)₂ and CaCO₃ present as impurities decompose to CaO. A carbonation step then proceeds while the vol % of CO₂ in the effluent gas is continuously registered by a gas analyzer. A subsequent calcination step is carried out up to complete decarbonation. A digital signal generator produces an electric sine wave of fixed frequency which is amplified by a power audio amplifier and excites a 8 W woofer loudspeaker. The acoustic vibration is driven to the reactor by means of a wave guide. The Sound Pressure Level (SPL) is sampled by a 1/4" condenser microphone.

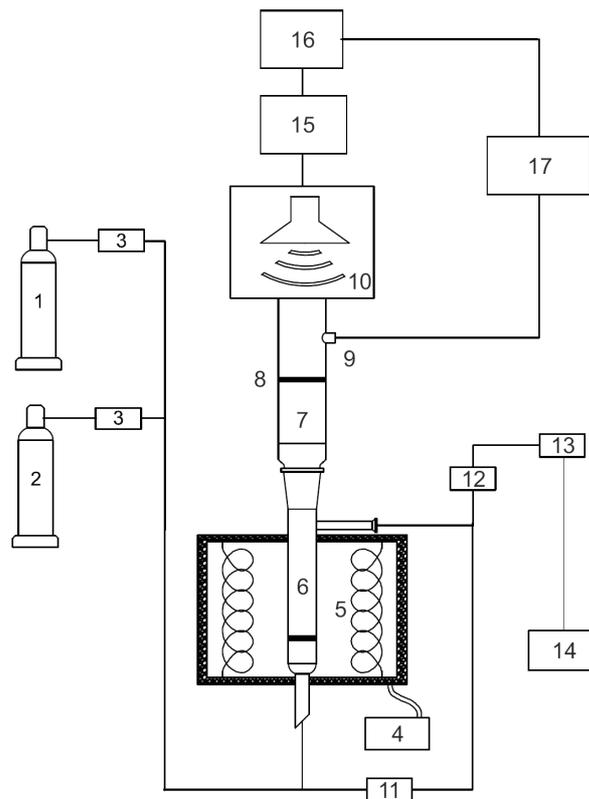


Figure 2: Sketch of the experimental setup. 1: Compressed gas used for carbonation (15% CO₂/85% N₂ vol/vol). 2: Compressed gas used for calcination (dry air). 3: Mass flow controllers. 4: Temperature controller. 5: Oven. 6: Quartz reactor. 7: Sound wave guide. 8: Elastic membrane. 9: Microphone. 10: Loudspeaker. 11: Differential pressure transducer. 12: Particle filter. 13: Mass flow meter. 14: Gas analyzer. 15: Signal amplifier. 16: Signal generator. 17: Oscilloscope.

Measurements of the differential gas pressure Δp across the powder at ambient temperature (taken between a point just above the gas distributor plate and atmospheric pressure) were performed by using a 40 mm i.d. polycarbonate cell. The purpose of these tests was to assess the fluidization behavior of the powder as affected by acoustic vibrations. Typically, it is $\Delta p \sim W$, where W is the material weight per unit area, for uniform fluidization.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 3 shows Δp vs. gas flow for fresh CaO, which exhibits in ordinary conditions a cohesive heterogeneous fluidization (Geldart C behavior). Once the gas velocity reaches a value sufficiently large to fluidize the bed, Δp takes a maximum value notably smaller than W and displays strong oscillations due to the development of channels through which the gas finds a bypass indicating very poor gas/solids contact efficiency. On the other hand, Fig. 3 demonstrates that acoustic vibrations serve to smooth the fluctuations of Δp , which now reaches a plateau that approaches W as either the sound intensity level (SPL) or frequency f are increased being the effect of sound intensity more marked. Visually, it is observed that gas channels are destabilized, the bed is expanded and gas-solids mixing uniformity is improved.

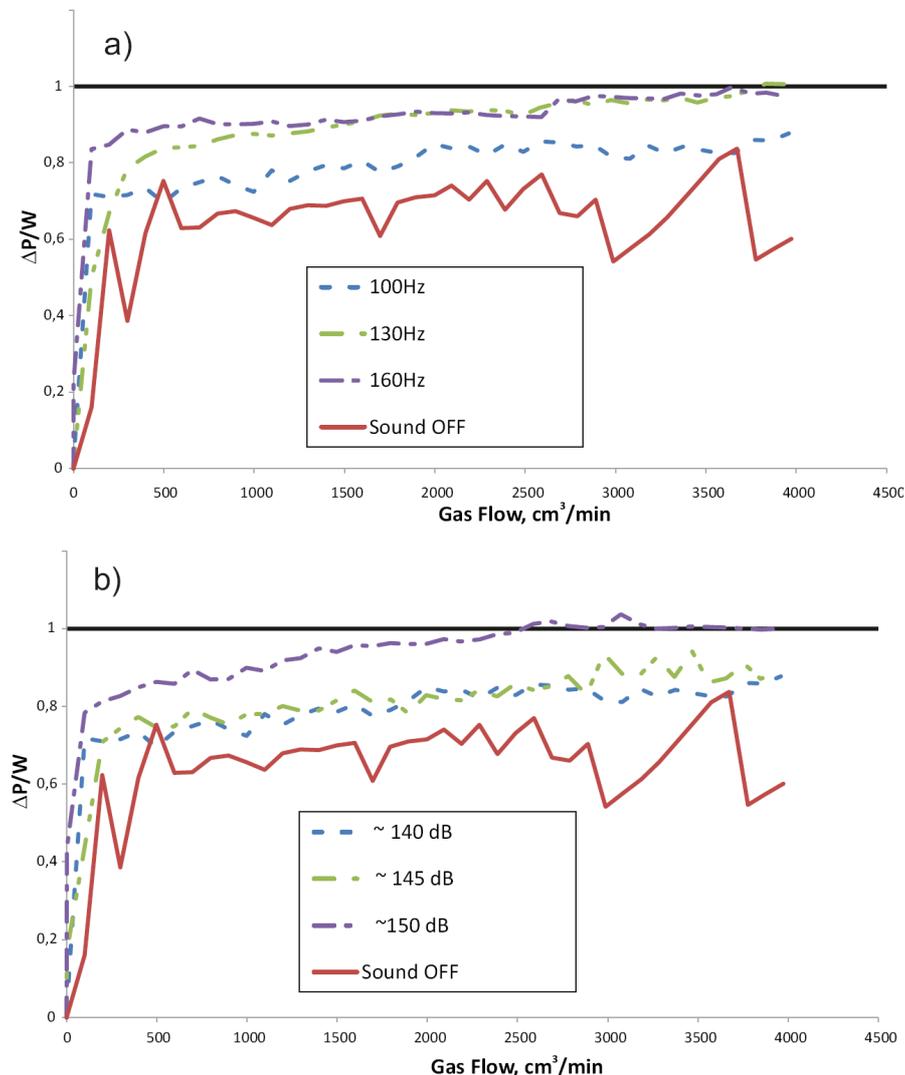


Figure 3: Differential gas pressure between the bottom of the bed and ambient atmosphere (made nondimensional with the material weight per unit area $W=513$ Pa) vs. gas velocity as affected by acoustic vibrations applied of different intensities and

frequencies (indicated). In a) the SPL is fixed to 140 dB. In b) the frequency is fixed to 100 HZ.

CO₂ breakthrough curves as affected by acoustic vibration are plotted in Fig. 4. As can be observed, application of sound causes a significant drop of the %CO₂ measured in the effluent gas during the first minutes of carbonation (fast phase). Moreover, there is a clear correlation between the enhancement of CO₂ capture in the fast phase, which is determined by the gas/solids contact efficiency, and the improvement of fluidization uniformity (as seen in Fig. 3). In both cases the main effect is observed when the sound intensity is increased while the effect of frequency is less relevant. Note also that the CO₂ breakthrough curves tend to converge at t ~ 50 min when %CO₂ ~ 10%. This suggests that from this point, CO₂ sorption becomes ruled by a slower process in which the gas-solids contact efficiency is not a determinant factor.

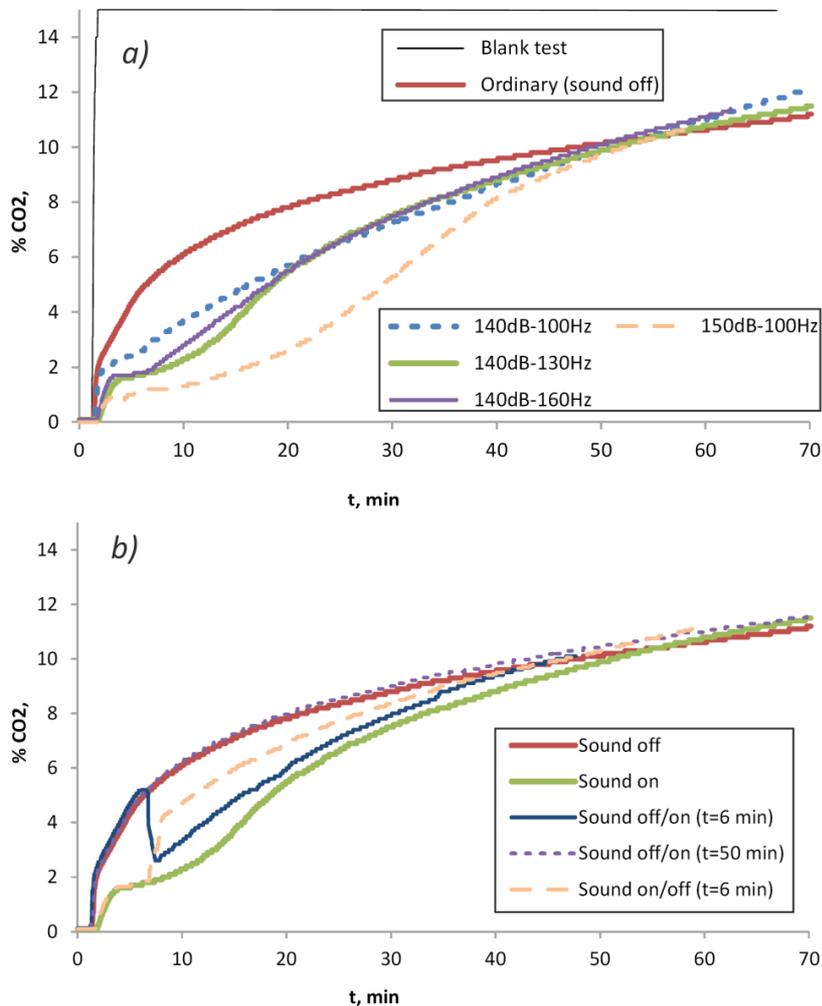


Figure 4: a) CO₂ vol % in the effluent gas of the fluidized bed (gas flow 2000 cm³/min) measured during carbonation as affected by acoustic vibration applied of different intensities and frequencies (indicated). Results from blank tests (empty cell) are also shown. In b) CO₂ breakthrough curves obtained by turning on/off the acoustic vibration (140 dB, 130 Hz) are plotted.

Figure 4b shows CO₂ breakthrough curves obtained by turning on/off the acoustic vibration during carbonation. Turning on acoustic vibration at $t \sim 6$ min yields a marked drop of the %CO₂ while turning it off gives rise to an increase of the %CO₂. Note, however, that in this latter case the CO₂ breakthrough curve keeps well below the curve obtained for the ordinary test in spite that the sound had been turned off. This indicates that the acoustic vibration applied during the first minutes of carbonation preconditions the material behavior likely by irreversibly disrupting particle aggregates and improving fluidization uniformity.

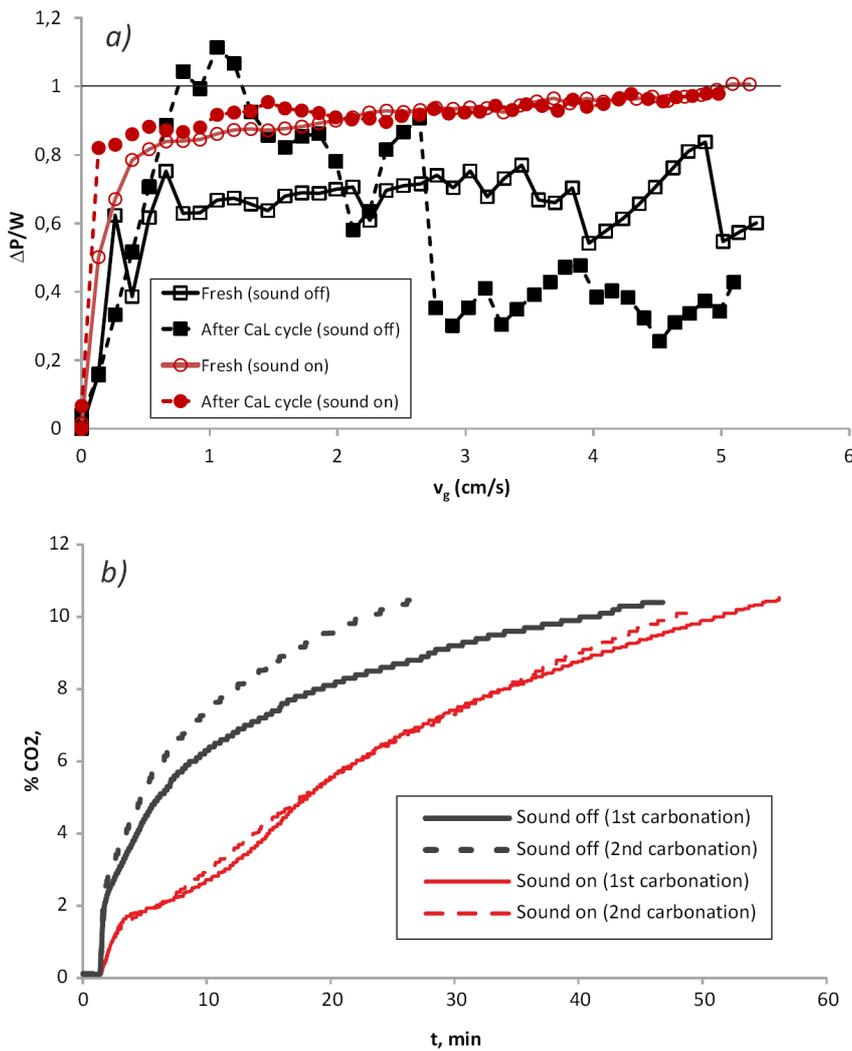


Figure 5: a) Differential gas pressure between the bottom of the bed and ambient atmosphere (made nondimensional with the material weight per unit area $W=513$ Pa) vs. gas velocity for fresh CaO and for CaO after being subjected to 1 calcination/carbonation cycle. Results are shown for tests performed in the absence of acoustic vibration and with acoustic vibration applied (140 dB, 130 Hz). b) CO₂ breakthrough curves obtained during the carbonation phases of 2 calcination/carbonation cycles carried out successively in the absence of acoustic vibration and with acoustic vibration applied (140 dB, 130 Hz).

Figure 4b shows that application of sound when %CO₂=10% (t=50 min) does not affect the subsequent evolution of the CO₂ breakthrough curve. At this slow carbonation stage, CO₂ sorption is no longer controlled by the gas/solids contact efficiency but by the diffusion of CO₂ through the carbonate layer on the particles' surface and the interior of the particle aggregates. Thus, it is explainable that turning on sound when carbonation has reached the slow stage does not yield a remarkable effect.

Gas pressure drop curves for the material after being subjected to the final calcination step are plotted in Fig. 5. As indicated by the large fluctuations of Δp , the level of fluidization heterogeneity exhibited by the cycled CaO has further increased as compared to the fresh CaO. Note also in Fig. 1 that the particle size distribution of a sample dispersed in isopropanol and ultrasonicated is shifted to smaller particle sizes due to its loss of mechanical strength, which makes the material more cohesive after 1 carbonation/calcinations cycle. Nevertheless, application of acoustic vibrations on the cycled material serves to recover the material fluidizability. Gas pressure drop curves for the fresh and cycled materials subjected to acoustic vibrations are similar (Fig. 5a), which leads us to expect that acoustic vibrations would serve not only to enhance the fast CO₂ capture capacity during a 1st carbonation stage but also to improve the material regenerability after being cycled. This is confirmed by the CO₂ breakthrough curves obtained for 2 calcination/carbonation cycles which were performed successively. As can be observed in Fig. 5b, the CO₂ capture performance in the 2nd cycle carried out in the absence of sound has considerably worsened as might be expected from the increase of fluidization heterogeneity. On the other hand, application of acoustic vibrations yields a similar CO₂ breakthrough curve for the second carbonation, i.e. the fast capture capacity of the first cycle is almost maintained in the second cycle.

CONCLUSIONS

In summary, the results shown in this work suggest that application of acoustic vibrations would be an effective method to enhance the efficiency of the CaL technology for CO₂ capture. It is seen that the enhancement of CO₂ capture is directly correlated to the improvement of fluidization uniformity. Other methods to homogenize fluidization of proven efficiency at laboratory scale are the use of additives to reduce cohesiveness, application of mechanical agitation, centrifugation, application of variable electric/magnetic fields, and injection of high velocity jets. While application of these methods might also lead to an improvement of the CO₂ capture performance, some of them are invasive or require material modification, and, in general, their use at the industrial level would require important modifications of the fluidized bed reactor design. On the other hand, application of acoustic vibrations does not require any material modification; it is rather cheap and can be easily implemented from the technical point of view. For example, there exists the possibility of using simple sound generator devices such as a pneumatic sonic generator through which part of the

gas stream is passed without requiring any additional consumption of energy (Komarov et al (6)). Moreover, the efficiency of acoustic vibrations on enhancing diverse gas-solids processes in fluidized bed reactors has been already demonstrated, as for example in combustion, pyrometallurgical, and pollutant filtration (Komarov et al. (6)). In these processes, application of sound results in an increase of the mass/heat transfer efficiency even though fluidized beds are operated in diverse regimes (bubbling or circulating fluidized beds) indicating that acoustic vibrations play a general role on promoting the efficiency of gas/solid processes. Accordingly, acoustic vibrations would be expected to yield also an enhancement of the CO₂ capture performance of Ca-based materials used in practice (namely, natural limestones) at CaL conditions and at the industrial level. Nonetheless pilot-scale tests remain to be carried out to confirm whether applying acoustic vibrations has beneficial effects to be implemented in the CaL technology. Furthermore, other phenomena that might be affected by acoustic vibrations and are relevant in practice such as attrition and elutriation should be assessed.

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